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Membrane-based Separations for Low-effluent Concepts

P.H. Pfromm

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MEMBRANE-BASED SEPARATIONS FOR LOW-EFFLUENT CONCEPTS

Peter H. Pfromm
Assistant Professor
Institute of Paper Science and Technology
Atlanta, GA 30318

ABSTRACT

Selective purging of materials such as chloride, metal ions, and hazardous air pollutants is vital for low-effluent mill strategies. Membrane separation processes such as electrodialysis, bipolar electrodialysis, vapor permeation, and pervaporation will be discussed as possible methods.

Electrodialysis is a continuous separation process to remove ions from aqueous streams. Industrial applications include demineralization in the food industry, drinking water purification, effluent treatment for metal plating, and boiler water pretreatment. A recently commercialized technique is bipolar electrodialysis. Removal of chloride and potassium from liquors and control of inorganics for low-effluent white water cycles are being investigated at IPST.

Emissions in the form of vapors and gases will have to be dealt with for true low emission mill operation. Separation of low molecular weight organics from aqueous or gaseous mixtures can be achieved with high selectivity by membrane permeation. The process is continuous and no spent adsorbents need to be dealt with. This technology is the subject of a joint project at IPST and Georgia Tech.

DISCUSSION

Membrane Separations: Porous vs. Non-Porous

Membrane separations can be divided into two groups. Porous membranes allow selective separation of objects ranging in size from particulates (~several micrometers) down to the size of dissolved organic molecules, and hydrated inorganic ions (nanofiltration, ~0.001 micrometers). At the extreme end of this "sieving scale" is reverse osmosis, where virtually all dissolved ions are retained, while water passes through the membrane. Generally, a large portion of a feed stream (>90%) will pass through the membrane under a hydrostatic pressure gradient. Certain particles or molecules in the feed stream will be rejected by the membrane. Selectivity depends on the pore size and distribution. Productivity depends on the surface porosity of the membrane, and on fouling resistance.

A second and more recently developed group of membrane separations uses non-porous membranes. Non-porous as used here means, for example, a polymer film with no defects on

the molecular scale. Even a single helium atom could not pass through this film, without interacting with the polymer matrix. Every defect on a molecular level is detrimental to the function of these membranes. No convective fluid flow through the membrane takes place. The driving force can be an electrical potential difference (ions in solution), or a partial pressure difference. Feed streams can be permanent gases, vapors, or liquids. The vast majority of the feed stream does not pass through the membrane. A small fraction of the molecules or atoms in the feed stream (contaminants, or a product to be recovered) passes through the membrane. The selectivity of this process is based on strong molecular interactions with the membrane material. Instead of sieving, as for the first group of separations, the mechanism of solution/diffusion provides selectivity.

In summary, the more recent developments in membrane separations have taken place for membranes that are non-porous (defect-free). Molecular interactions provide selectivity. Fouling issues are quite different from porous membrane separations (filtration), since only a small fraction of feed stream material passes through the membrane.

Electrodialysis

Removal of inorganics from recycle streams

In electrodialysis of aqueous solutions, ions pass through ion-exchange membranes. The membrane material is generally similar to conventional ion exchange resins. For recycling of liquid streams in pulp and paper production, the removal of inorganics that enter the process with the water, makeup chemicals, additives, and the wood is important. Paper machine white water mineral levels, for example, are expected to rise dramatically if closure is attempted. Among other problems, scaling, corrosion, and decreased retention were observed (Gremban, 1986; Bowers, 1977; Heller et al., 1979). The composition of white water can include anionic or cationic organic molecules, ranging from polymeric additives with high charge density to lignin fragments. This stream was chosen to evaluate electrodialysis for mineral removal in closed cycle concepts due to its complexity. Figure 1 shows a process schematic for continuous removal of inorganics from white water.

The basic principles of fouling are the subject of ongoing work at IPST. A model white water inorganic composition was derived from data in the literature. Electrodialysis experiments with conventional membranes showed an increased electrical resistance when sulfonated lignin was present.

The total electrical resistance of a laboratory scale electrodialysis stack that was run with model white water with and without sulfonated lignin present (inorganic: 1000 ppm, organic: 4000 ppm sulfonated lignin added) is shown in

Figure 2. Increasing mass transfer resistance due to salt removal is clear in all cases. However, interaction of organics with the membranes can be deduced from the additional resistance increase when organics are present. These results confirm that dissolved lignosulfonates will influence the electrodialysis process negatively. When the main fouling mechanisms are clear, measures such as surface modifications can be taken to allow continuous and efficient electrodialysis of white water.

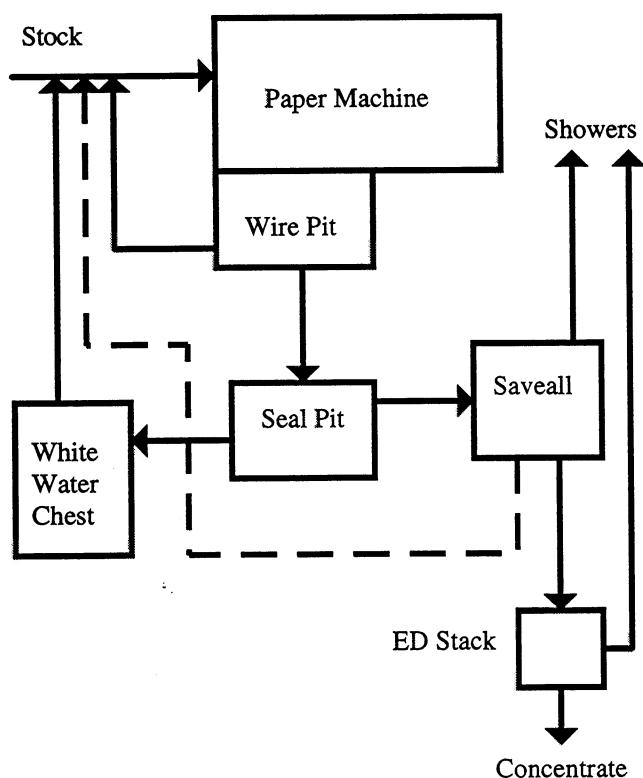


Figure 1: Electrodialysis for continuous removal of inorganic dissolved solids from a closed white water cycle (dashed line: solids from saveall).

Costs on the order of \$0.1/m³ of water treated have been reported for industrial-scale electrodialysis in the white water concentration range. The process is reported to be far more economical for this task than evaporation or reverse osmosis.

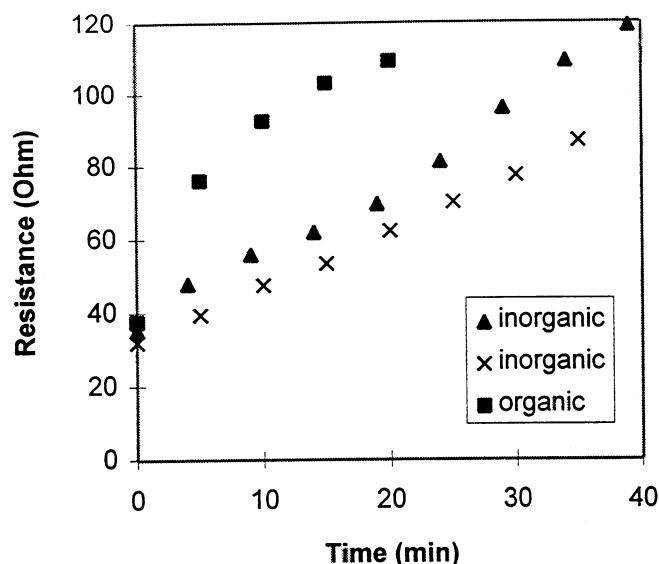


Figure 2: Electrical resistance of an electrodialysis stack for demineralization of model white water, with and without dissolved organics present (4 diluate cells, conventional anion/cation exchange membranes).

Chloride removal

Chloride removal from bleach plant effluent has been suggested (Gransson et al., 1995). The issue of organic fouling, as shown above, is vital for use of the technology. Pretreatments such as adsorption or flocculation to remove organics will greatly increase operating costs and complexity. Chloride can be separated selectively from mixtures such as dissolved ESP catch, using monovalent-selective ion exchange membranes (Maruko, 1980). Again, this is a highly attractive method if the issue of organic fouling can be handled. Clearly, the goal must be membrane lifetimes on the order of years without significant losses in productivity. This chloride removal process has a dual payback: saltcake is recovered to reduce makeup chemical costs and recovery boiler plugging and deadload are reduced (Tran, 1986).

Vapor Permeation

The removal of organics such as hydrocarbons or chlorinated hydrocarbons from liquid and vapor streams has recently been commercialized (Wijmans et al., 1987; Ohlrogge et al., 1990). This is another example of membrane separations with non-porous membranes. A feed stream, for example, air laden with methanol, is passed across a non-porous polymeric membrane. This membrane is non-porous, has a thickness of a few thousand angstrom, and is commercially packaged in hollow fiber or spiral wound modules. The thin selective layer must be produced without defects on a molecular scale. Defects on the order of a few ppm of the surface area destroy the selectivity.

The selective removal of methanol from vapor streams is being investigated. Choices for optimum polymers will be made based on sorption and diffusion measurements. The process is continuous, and no waste materials (adsorbents etc.) are produced. This process can be an alternative to treat certain point sources, rather than installing systems to collect and treat all vapor streams at a central location.

SUMMARY

Membrane separations that rely on solution/diffusion as the selective transport mechanism can be highly selective to remove minority components from liquids, vapors, or gases. Examples are inorganic ions from aqueous solutions, such as minerals from closed white water cycles, and chloride from the pulping operation.

REFERENCES

- Maruko, S., "Method of Dechlorination," Jap. Pat. 22,051/80 (1980).
- Tran, H. N., "How does a recovery boiler become plugged?," *Tappi Journal*, 69(11): 102 (1986).
- Gransson, G., Sundblad, B., Landfors, J., Baltsn, H. A., "Method for purifying process water from pulp manufacture," U. S. Pat. 5,437,791 (1995).
- Wijmans, J.G., Baker, R.W., Kuroda, T., Pfromm, P.H., Peinemann, K.-V., Burnett, L.J., Haesloop, D. J., "Separation of Organic Vapors from Air with Membranes," AIChE Meeting, Miami Beach, Florida, Paper 128D, November 1986.
- Ohlrogge, K. and K.-V. Peinemann, "The Separation of Hydrocarbons with Membranes," *Separation Science and Technology*, 25(): 1375 (1990).
- Gremban, E. G., "Water Reuse Program," Tappi Papermakers Conference Proceedings, p. 93 (1986).
- Bowers, D. F., "Effect of closed water systems and cleaning procedures on corrosion of papermaking equipment," *Tappi Journal*, 60(10): 57 (1977).
- Heller P., Scott W. E., Springer A. M., "Potential operational problems under conditions of complete water reuse," *Tappi Journal*, 62(12):79 (1979).

